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FINAL REPORT

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By

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Title: High Resolution Spectroscopy to Support Atmospheric Measurements

The major research activities performed during the cooperative agreement enhanced our spectroscopic knowledge of molecules of atmospheric interest such as H_2O (water vapor), O_3 (ozone), HCN (hydrogen cyanide), CH_4 (methane), NO_2 (nitrogen dioxide) and CO (carbon monoxide). The data required for the analyses were obtained from two different Fourier transform spectrometers (**FTS**); one of which is located at the National Solar Observatory (NSO) on Kitt Peak, Arizona and the other instrument is located at the Pacific Northwest National Laboratories (PNNL) at Richland, Washington. The data were analyzed using a modified multispectrum nonlinear least squares fitting algorithm developed by Dr. D. Chris Benner of the College of William and Mary [1]. The results from these studies made significant improvements in the line positions and intensities for these molecules. The measurements of pressure broadening and pressure induced line shift coefficients and the temperature dependence of pressure broadening and pressure induced shift coefficients for hundreds of infrared transitions of HCN, CO, C H_4, and H_2O were also performed during this period. Results from these studies have been used for retrievals of stratospheric gas concentration profiles from data collected by several Upper Atmospheric Research satellite (**UARS**) infrared instruments as well as in the analysis of high resolution atmospheric spectra such as those acquired by space-based, ground-based, and various balloon- and aircraft-borne experiments. Our results made significant contributions in several updates of the HITRAN (HIgh resolution TRANsmission) spectral line parameters database. This database enjoys worldwide recognition in research involving diversified scientific fields.

The research conducted during the period 2003-2006 has resulted in the following publications. In addition to Journal publications, several oral and poster presentations were given at various Scientific conferences within the United States and abroad.

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1. D. Chris Benner, C.P. Rinsland, V. Malathy Devi, M.A.H. Smith, D. Atkins, A multispectrum nonlinear least squares fitting technique, J. Quant. Spectrosc. Radiat Transfer, 53(1995) 705-721.

Brief descriptions of the various projects:

1. CH_4 (methane): Methane is a molecule of importance to atmospheric studies. Due to the high methane abundance (~1.6 ppmv) in the atmosphere, even lines belonging to isotopic methane (such as $^{13}CH_4$ and $^{12}CH_3D$) contribute significant absorption in many regions of atmospheric spectra. Accurate measurements of spectroscopic parameters such as pressure-broadening coefficients, pressure- induced line-shift coefficients, line mixing coefficients and their temperature dependence are needed for accurate simulations of methane features in atmospheric spectra.

Pressure broadening coefficients of $^{12}CH_4$, $^{13}CH_4$ and $^{12}CH_3D$ molecules in several spectral regions including the fundamental, combination and overtone bands have been determined using spectra recorded with FTS instruments.

Accurate laboratory measurements of positions, intensities, pressure broadening and pressure induced shift coefficients of CH_3D lines are crucial for quantitative analysis (e.g., determination of CH_3D abundance and D/H ratio) of the spectral signatures of this molecule observed in the terrestrial and planetary atmospheres. The multispectrum fitting technique capable of interpreting the line mixing effects have successfully been applied in the analyses of the triad region (ν_3, ν_5 and ν_6 bands) of $^{12}CH_3D$ in the 6-10μm spectral region.

The analyses of methane spectra recorded at 0.011 cm^{-1} resolution in the following MOPITT (Measurements Of Pollution In The Troposphere) spectral regions: 4265-4305 cm^{-1} (the MOPITT CO channel) and 4350-4500 cm^{-1} (the MOPITT CH_4 channel) have been completed and the results are reported in two Journal articles . These two spectral channels are part of the crowded methane "octad region" containing eight overtone and combination bands. These spectra were recorded using the MaMath-Pierce FTS. Using the multispectrum fitting technique we have measured accurate line intensities, self- and air-broadened half width and pressure shift coefficients for more than 1000 methane transitions.

The analysis of the Q branch of the ν_4 band of methane was begun. The analysis is not yet

methane was begun. The analysis is not yet completed, but still in progress. However, an oral presentation of the work done was given at the 60th Ohio State University International Symposium on Molecular Spectroscopy, held in June 2005.

2. NO_2:

Nitrogen dioxide (NO_2) is an atmospheric pollutant involved in the production and destruction of ozone. Produced by oxidation of NO, it is the main source of ozone in the troposphere and a precursor of nitric acid. Atmospheric NO_2 is continually monitored to determine its global distribution and sources and sinks in the atmosphere. In order to perform systematic measurements via spectroscopic remote sensing techniques at wavelengths ranging from the microwave through the infrared to the ultraviolet accurate and complete knowledge of NO_2 spectroscopy is required.

We recorded several spectra of NO_2 and NO_2 broadened with air at various temperatures and measured line positions, air broadened widths and shift coefficients and their temperature dependences. The HITRAN database was updated with a new line list based upon our measurements

3. H_2O (water): Water vapor plays a crucial role in atmospheric chemistry. Many remote sensing experiments utilize the pure rotation and vibration-rotation bands of water vapor for soundings of H_2O in the Earth's atmosphere. Using our heatable multipass absorption cell, we have recorded 'hot' water spectra to determine the variation of the width and shift coefficients of water vapor lines (broadened with foreign gases such as air) in the ν_2 fundamental band near the 6-μm spectral region.

4. CO (carbon monoxide): Given the increasing level of sophistication in remote sensing instrumentation, there is a need for accurate spectroscopic data relevant to planetary atmospheres such as Jupitar. Compared to the large number of papers published on line parameters in pure CO, there are relatively very few studies on measurements of broadening and pressure-induced shifts in CO perturbed by H_2 (hydrogen). From analyzing high resolution room temperature laboratory absorption spectra values for self-broadened and hydrogen broadened Lorentz width coefficients and self- and hydrogen pressure-induced shift coefficients have been measured for a number of

transitions in the 2←0 band of $^{12}C^{16}O$. These studies also enabled us to verify that our measurement and analysis techniques gave results consistent with those of other spectroscopic laboratories.

5. HCN (hydrogen cyanide).

Air– and N_2–broadening, air– and N_2–pressure–induced shift coefficients and the temperature dependence exponent of the broadening coefficients and the temperature dependent coefficient of pressure–induced shifts have been determined for transitions of the ν_1 band of $H^{12}C^{14}N$ from 39 laboratory absorption spectra recorded at 0.005 and 0.008–cm^{-1} resolutions with two different Fourier transform spectrometers. The parameters were retrieved from the multispectrum nonlinear least squares fits to the 3200– to 3400– cm^{-1} region of spectra recorded at temperatures between $+26^0C$ and -60^0C. Line parameters for N_2 broadening were determined by fitting 27 spectra simultaneously while air-broadening parameters were quantified from simultaneous fits to 22 spectra. Similar measurements with air as the broadening gas were performed in the ν_2 and 2 ν_2 bands of HCN.

In addition to above specific tasks, studies on other molecules were also performed.

Several Journal publications have resulted from analyses of the spectra of these molecules during the funding period. The following list provides the activities carried out in 2003-2004, 2004-2005 and 2005-2006, respectively.

Publications and presentations in 2003-2004:

Journal Publications:

1. V. Malathy Devi, D. Chris Benner, M.A.H. Smith, C.P. Rinsland, S.W. Sharpe, R.L. Sams.A multispectrum analysis of the ν_1 band of $H^{12}C^{14}N$. I. Intensities, self-broadening and self-shift coefficients, J. Quant. Spectrosc. Radiat. Transfer, 82, 319-341, (2003).

temperature dependences, J. Quant. Spectrosc. Radiat. Transfer, 82, 343-362, (2003).

3. C.P. Rinsland, J.-M. Flaud, A. Perrin, M. Birk, G. Wagner, A. Goldman, A. Barbe, M.R. De Backer-Barilly, S.N. Mikhailenko, V.G. Tyutererv, M.A.H. Smith, V. Malathy Devi, D. C. Benner, F. Schreier, K.V. Chance, J. Orphal, T.M. Stephen, Spectroscopic parameters for ozone and its isotopes: Recent measurements, outstanding issues, and prospects for improvements to HITRAN, J. Quant. Spectrosc. Radiat. Transfer, 82, 207-218, (2003).

4. L.S. Rothman, A. Barbe, D.C. Benner, L.R. Brown, C. Camy-Peyret, M.R. Carleer, K.V. Chance, C. Clerbaux, V. Dana, V. malathy Devi, A. Fayt, J.-M. Flaud, R.R. Gamache, A. Goldman, D. Jacquermart, K.W. Jucks, W.J. Lafferty, J.-Y. Mandin, S.T. Massie, V. Nemtchinov, D.A. Newnham, A. Perrin, C.P. Rinsland, J. Schroeder, K.M. Smith, M.A.H. Smith, K. Tang, R.A. Toth, J. Vander Auwera, P. Varanasi, K. Yoshino, The HITRAN molecular spectroscopic database: Edition of 2000 including updates through 2001, J. Quant. Spectrosc. Radiat. Transfer, 82, 5-44 (2003).

5. M. Lepere, R. Gobeille, N. Kolodziejski, V. Malathy Devi, D. C. Benner, M.A.H. Smith, W. McMichael, B. Aoaeh, K. Wilkinson, A.W. Mantz, Analysis of tunable diode laser spectra of $^{R}Q(J,0)$ lines in CH_3F near 1475 cm^{-1} using a multispectrum fitting technique, J. Mol. Spectrosc. 224, 7-12 (2004).

6.V. Malathy Devi, D.Chris Benner, M.A.H. Smith, C.P. Rinsland, S.W. Sharpe, R.L. Sams, A multispectrum analysis of the $2\nu_2$ spectral region of $H^{12}C^{14}N$: Intensities, broadening and pressure-shift coefficients. J. Quant. Spectrosc. Radiat. Transfer, 87, 339-366 (2004).

List of Conference presentations:

1.Self- and air-broadening and shifting of methane in the 4200-4500 cm^{-1} spectral range, A. Predoi-Cross, V. Malathy Devi, D. Chris Benner, Linda Brown, paper presented at the 58th Ohio State University International Symposium on Molecular Spectroscopy, June 16-20, 2003, **paper MG11**.

2.Temperature dependence of air-broadened line widths and shifts of water at 6mm, R.A. Toth, L.R. Brown, M.A.H. Smith, V. Malathy Devi, D. Chris Benner, , paper presented at the 58th Ohio State University International Symposium on Molecular Spectroscopy, June 16-20, 2003, **paper TA01**.

3. Multispectum analysis of the ν_1 band of HCN: intensities, broadening and shift coefficients, V. Malathy Devi, D. Chris Benner, M.A.H. Smith, C.P. Rinsland, S.W. Sharpe, R.L. Sams, , paper presented at the 58th Ohio State University International Symposium on Molecular Spectroscopy, June 16-20, 2003, **paper TA02.**

4. Intensities, self- and air-broadening, and pressure-induced line shifts in the 2nu2 band of HCN, V. Malathy Devi, D. Chris Benner, M.A.H. Smith, C.P. Rinsland, S.W. Sharpe, R.L. Sams, paper presented at the 58th Ohio State University International Symposium on Molecular Spectroscopy, June 16-20, 2003, **paper TA03**.

Publications and presentations in 2004-2005:

Journal publications:

1. L.R. Brown, A. Nikitin, D.C. Benner, V. Malathy Devi, M.A.H. Smith, L. Fejard, J.P. Champion, V.G. Tyuterev, R.L. Sams, Line intensities of CH_3D in the triad region: 6-10μm. Journal of Moecular Structure., 695-696, 181-188 (2004).

2. V. Malathy Devi, A. Predoi-Cross, D. Chris Benner, M.A.H. Smith, C.P. Rinsland and A.W. Mantz, Self- and H_2-broadened width and shift coefficients in the 2←0 band of $^{12}C^{16}O$: Revisited, J. Mol. Spectrosc, 228, 580-592 (2004).

3. D. Chris Benner, T.A. Blake, L.R. Brown, V. Malathy Devi, M.A.H. Smith and R.A. Toth, Air-broadening in the ν_3 band of $^{14}N^{16}O$ using a multispectrum fitting technique, J. Mol. Spectrosc. 228, 593-619 (2004).

4. L.S. Rothman, D. Jacquermart, A. Barbe, D. Chris Benner, M. Birk, L.R. Brown, M.R. Carleer, C. Chackerian, Jr, K. Chance, V. Dana, V.M. Devi, J.-M. Flaud, R.R. Gamache, A. Goldman, J._M. Hartmann, K.W. Jucks, A.G. Maki, J.-Y. Mandin, S.T. Massie, J. Orphal, A. Perrin, C.P. Rinsland, M.A.H. Smith, J. Tennyson, R.N. Tolchenov, R.A. Toth, J. Van der Auwera, P. Varanasi, G. Wagner, The 2004 HITRAN Molecular Database, J. Quantitative Spectrosc. Radiat. Transfer, 96 (2005) 139-204

List of Conference presentations:

1. The ν_3 band of NO_2: Analysis technique, D. Chris Benner, V. Malathy Devi, L.R. Brown, R.A. Toth, M.A.H. Smith, paper presented at the 59th Ohio State University International Symposium on Molecular Spectroscopy, June 21-25, 2004, **paper RB05**.

2. Air-broadening parameters in the ν_2 band of $^{14}N^{16}O_2$ using a multispectrum fitting technique, D. Chris Benner, V. Malathy Devi, T.A. Blake, L.R. Brown, R.A. Toth, M.A.H. Smith, paper presented at the 59th Ohio State University International Symposium on Molecular Spectroscopy, June 21-25, 2004, **paper RB06**.

3. Self- and H_2-broadening and shift coefficients in the 2←0 band of $^{12}C^{16}O$: Revisited, V. Malathy Devi, D. Chris Benner, A. Predoi-Cross, M.A.H. smith, C.P. Rinsland, A.W. Mantz, paper presented at the 59th Ohio State University International Symposium on Molecular Spectroscopy, June 21-25, 2004, **paper RB09**.

4. Broadening and shift coefficients in the ν_2 band of HCN, M.A.H. Smith, C.P. Rinsland, V. Malathy Devi, D. Chris Benner, S.W. Sharpe, R.L. Sams, paper presented at the 59th Ohio State University International Symposium on Molecular Spectroscopy, June 21-25, 2004, **paper RB10**.

Publications and presentations in 2005-2006:

Journal publications

1. J.P. Bouanich, C. Boulet, A. Predoi-Cross, S.W. Sharpe, R.L. Sams, M.A.H. Smith, C.P. Rinsland, D. Chris Benner, V. Malathy Devi, A multispectrum analysis of the ν_2 band of HCN: Part II. Theoretical calculations of self-broadening, self-induced shifts, and their temperature dependences, J. Mol.Spectrosc. 231, 85-95 (2005)

2. L.R. Brown, D. Chris Benner, V. Malathy Devi, M.A.H. Smith and R.A. Toth, Line mixing in self- and foreign-broadened water vapor at 6 μm, Journal of Molecular Structure, 742, 111-122 (2005).

3. A. Predoi-Cross, L.R. Brown, V. Malathy Devi, M. Brawley-Tremblay, D. Chris Benner, Multispectrum analysis of $^{12}CH_4$ from 4100 to 4635 cm^{-1}: I. Self-broadening coefficients (Widths and shifts), J. Mol. Spectrosc. 232 (2005) 231-246,

Multispectrum analysis of $^{12}CH_4$ from 4100 to 4635 cm^{-1}: I. Self-broadening coefficients (Widths and shifts), J. Mol. Spectrosc. 232 (2005) 231-246,

4. A.W. Mantz, V. Malathy Devi, D. Chris Benner, M.A.H. Smith, A. Predoi-Cross, M. Dulick, A multispectrum analysis of widths and shifts in the 2010 to 2260 cm^{-1} region of $^{12}C^{16}O$ broadened by Helium at temperatures between 80 and 297 K, Journal of Molecular Structure 742 (2005) 99-110.

5. R.A. Toth, L.R. Brown, M.A.H. Smith, V. Malathy Devi, D. Chris Benner, M.Dulick, Air-broadening of H_2O as a function of temperature: 696-2163 cm^{-1}. J. Quant. Spectrosc. Radiat. Transfer (to appear in 2006).

List of Conference presentations:

1. Line widths and shifts in the 1←0 band of $^{12}C^{16}O$ broadened by helium at temperatures between ~80 and 297 K, A.W. Mantz, V. Malathy Devi, D. Chris Benner, M.A.H. Smith, A. Predoi-Cross, M. Dulick, paper presented at the 60th Ohio State University International Symposium on Molecular Spectroscopy, June 20-24, 2005, **paper TE02**.

2. Air-broadening line widths and shifts in the ν_3 band of 16O3 at temperatures between 160 and 300K, M.A.H. Smith, C.P. Rinsland, V. Malathy Devi, D. Chris Benner, A.M. Cox, paper presented at the 60th Ohio State University International Symposium on Molecular Spectroscopy, June 20-24, 2005, **paper TE03**.

3. Line mixing in self- and foreign-broadened water vapor, L.R. Brown, R.A. Toth, V. Malathy Devi, D. Chris Benner, M.A.H. Smith, paper presented at the 60th Ohio State University International Symposium on Molecular Spectroscopy, June 20-24, 2005, **paper TE07.**

4. Multispectrum analysis of methane from 4100 to 4635 cm-1: self- and air-broadening coefficients (widths and shifts), A. Predoi-Cross, L.R. Brown, V. Malathy Devi, D. Chris Benner, paper presented at the 60th Ohio State University International Symposium on Molecular Spectroscopy, June 20-24, 2005, **paper TE08**.

5. Line shapes in the Q branch of the ν_4 band of methane, D. Chris Benner, V. Malathy Devi, M. A.

H. Smith, L.R. Brown, paper presented at the 60th Ohio State University International Symposium on Molecular Spectroscopy, June 20-24, 2005, **paper TE09**.

6. Line mixing in self- and foreign-broadened water vapor, M.A.H. Smith, L.R. Brown, R.A. Toth, V. Malathy Devi, D. Chris Benner, Poster paper **(F13)** presented at the nineteenth colloquium on High-Resolution Molecular Spectroscopy in Salamanca (Spain), 11-16 September 2005.

7. Low-temperature line broadening, line shifts, and line shapes in the n4 band of methane, M.A.H. Smith, V. Malathy Devi, D. Chris Benner, L. R. Brown, Poster paper **(L11)** presented at the nineteenth colloquium on High-Resolution Molecular Spectroscopy in Salamanca (Spain), 11-16 September 2005.